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Structure of (Dithiopivalato)(trithioperoxypivalato)platinum(II), [Pt($C_5H_9S_2$)($C_5H_9S_3$)]

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Abstract. $M_r = 493{\cdot}66$, monoclinic, $C2/c$, $a = 18{\cdot}785\,(4)$, $b = 6{\cdot}204\,(2)$, $c = 27{\cdot}372\,(5)$ Å, $\beta = 95{\cdot}35\,(2)^\circ$, $V = 3176\,(1)$ Å^3, $Z = 8$, $D_m = 2{\cdot}04\,(2)$, $D_x = 2{\cdot}07$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 9{\cdot}867$ mm^{-1}, $F(000) = 1888$, room temperature, final $R = 0{\cdot}038$ for 1919 observed reflections. Four- and five-membered rings are present, with Pt—S bond distances of 2·322 (4), 2·323 (3) and 2·238 (4), 2·248 (3) Å respectively and an S—S bond of 2·037 (5) Å.

Introduction. In the course of our studies on metal chain compounds of Pt^{II} with dithiocarboxylic acid ligands (Bellitto, Flamini, Piovesana & Zanazzi, 1980; Bellitto, Dessy, Fares & Flamini, 1981), we observed that K_2PtCl_4 reacts with dithiopivalic acid in toluene under reflux to form the corresponding platinum(II) complex, the X-ray crystal structure of which is reported here.

Experimental. Dithiopivalic acid was prepared according to known procedures (Houben & Pohl, 1907; Beiner & Thuillier, 1972). The title compound was prepared by reaction of K_2PtCl_4 (4·82 mmol) and the ligand $(CH_3)_3CCS_2H$ (14·9 mmol) in toluene (100 ml). The mixture was refluxed under nitrogen for 3 d. The orange-red solution was then filtered and reduced in volume until a red oil was obtained, which was treated with hexane and the resulting solution cooled to 268 K. After 1 d, red-orange crystals were precipitated, filtered and collected. Analysis: calculated: Pt 39·53, C 24·34, H 3·65, S 32·48 wt%; found: Pt 39·44, C 24·48, H 3·68, S 32·40 wt%. ^{1}H NMR [CD_2Cl_2, $\delta(CH_3)_3C$ 1·72 and 1·38 p.p.m.]. D_m measured by flotation. Crystal 0·4 × 0·11 × 0·05 mm. Syntex $P2_1$ automated diffractometer, θ–2θ scan technique ($3^\circ \le 2\theta \le 50^\circ$), graphite-monochromated radiation. Cell constants: least-squares refinement of the setting angles of 15 computer-centred reflections in the range $19^\circ < 2\theta < 25^\circ$. Two standard reflections ($22\bar{6}$, $51\bar{3}$) recollected every 30 reflections: no significant change. Total of 3164 reflections collected; 1919 unique reflections ($R_{\text{int}} = 0{\cdot}063$) with $I \ge 3\sigma(I)$ were used (corrected for Lorentz and polarization effects) in the structure solution and in the refinement of 144 parameters (ratio data/parameters = 13·3). Semi-empirical absorption correction (North, Phillips & Mathews, 1968) based on a 360° ψ scan around the scattering vector of the $13\bar{3}$ reflection; max. value of the normalized correction factor 1·59. Structure solved by Patterson and Fourier techniques and refined by full-matrix least-squares method; $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1/\sigma(F_o)^2$. All non-hydrogen atoms assigned anisotropic temperature factors. A difference map, computed at an intermediate stage of the refinement, revealed maxima at the expected positions for all the H atoms, which were included in their idealized geometrical positions (C—H = 0·95 Å). R values converged to $R = 0{\cdot}038$ and $R_w = 0{\cdot}034$. In the final cycle of refinement, $(\Delta/\sigma)_{\max} < 0{\cdot}3$ and $(\Delta\rho)_{\max} = 0{\cdot}18$ e Å^{-3}. Calculations carried out on the HP-21MX computer of the Laboratorio di Strutturistica Chimica del CNR, Area della Ricerca di Roma, using the set of crystallographic programs developed by R. Spagna. Neutral atomic scattering factors (f' and f'' values) from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are in Table 1, bond distances and angles in Table 2.* The crystal structure consists of discrete molecules, whose structure is shown in Fig. 1. The Pt atom is coordinated, in a tetrahedrally distorted square-planar arrangement, by four S atoms belonging to two different, four- and five-membered chelate rings, both lying on the same plane. The S—Pt—S angles within the two rings are 73·0 (1) and 93·6 (1)°, and correspondingly two different Pt—S bond lengths are found, *i.e.* 2·323 (4) and 2·242 (4) Å (mean values) respectively. These can be compared with those found in other analogous PtS_4 chromophores containing four- or five-membered rings (Fackler & Thompson, 1981; Dessy & Fares, 1980; Dessy, Fares, Bellitto & Flamini, 1982).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39087 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$), *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt(1)	1159 (1)	2101 (1)	1183 (1)	41 (1)
S(1)	1477 (2)	4937 (7)	694 (1)	57 (2)
S(2)	957 (2)	968 (6)	374 (1)	57 (2)
S(3)	792 (3)	−964 (6)	1510 (1)	63 (2)
S(4)	1433 (2)	3664 (6)	1918 (1)	52 (2)
S(5)	933 (2)	−561 (6)	2251 (1)	57 (2)
C(1)	1248 (7)	3403 (23)	204 (5)	49 (8)
C(2)	1277 (8)	4046 (27)	−325 (5)	57 (8)
C(3)	636 (14)	5407 (58)	−482 (8)	134 (20)
C(4)	1398 (26)	2306 (50)	−649 (8)	186 (30)
C(5)	1896 (20)	5650 (69)	−353 (9)	157 (26)
C(6)	1263 (7)	1903 (26)	2365 (4)	50 (7)
C(7)	1392 (7)	2581 (18)	2908 (4)	43 (7)
C(8)	758 (10)	3977 (31)	3026 (6)	70 (10)
C(9)	1461 (14)	666 (34)	3243 (6)	92 (13)
C(10)	2078 (11)	3893 (35)	2993 (6)	81 (12)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Pt–S(1)	2·322 (4)	C(1)–C(2)	1·51 (2)
Pt–S(2)	2·323 (3)	C(2)–C(3)	1·50 (3)
Pt–S(3)	2·238 (4)	C(2)–C(4)	1·43 (3)
Pt–S(4)	2·248 (3)	C(2)–C(5)	1·54 (3)
S(1)–C(1)	1·667 (13)	C(6)–C(7)	1·54 (1)
S(2)–C(1)	1·687 (14)	C(7)–C(8)	1·53 (2)
S(3)–S(5)	2·037 (5)	C(7)–C(9)	1·50 (2)
S(4)–C(6)	1·694 (13)	C(7)–C(10)	1·52 (2)
S(5)–C(6)	1·668 (15)		

S(1)–Pt–S(2)	73·0 (1)	C(1)–C(2)–C(3)	109 (1)
S(3)–Pt–S(4)	93·6 (1)	C(1)–C(2)–C(4)	115 (1)
Pt–S(1)–C(1)	88·3 (5)	C(1)–C(2)–C(5)	108 (1)
Pt–S(2)–C(1)	87·9 (4)	C(6)–C(7)–C(8)	107 (1)
Pt–S(3)–S(5)	106·1 (2)	C(6)–C(7)–C(9)	112 (1)
Pt–S(4)–C(6)	109·0 (5)	C(6)–C(7)–C(10)	110 (1)
S(3)–S(5)–C(6)	108·1 (4)		
S(4)–C(6)–S(5)	123·2 (7)		

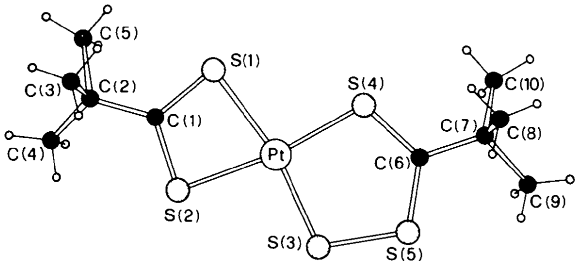

Fig. 1. A perspective view of the molecular structure with the labelling scheme.

Similar results have been observed in the analogous (dithiocumato)(trithioperoxycumato)platinum(II) by Fackler (1983).

Finally, the *tert*-butyl group does not seem to have any influence on the geometry of the rings and it behaves like the aryl substituent in the easy formation of dithio–trithio complexes.

References

BEINER, J. M. & THUILLIER, A. (1972). *C. R. Acad. Sci. Sér. C*, **274**, 642.

BELLITTO, C., DESSY, G., FARES, V. & FLAMINI, A. (1981). *J. Chem. Soc. Chem. Commun.* pp. 409–411.

BELLITTO, C., FLAMINI, A., PIOVESANA, O. & ZANAZZI, P. F. (1980). *Inorg. Chem.* **19**, 3632–3636.

DESSY, G. & FARES, V. (1980). *Acta Cryst.* B**36**, 2266–2269.

DESSY, G., FARES, V., BELLITTO, C. & FLAMINI, A. (1982). *Cryst. Struct. Commun.* **11**, 1743–1745.

FACKLER, J. P. (1983). Private communication.

FACKLER, J. P. & THOMPSON, L. D. (1981). *Inorg. Chim. Acta*, **48**, 45–52.

HOUBEN, J. & POHL, H. (1907). *Chem. Ber.* **40**, 1303–1307.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–103. Birmingham: Kynoch Press.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS F. S. (1968). *Acta Cryst.* A**24**, 351–359.

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trans-(Acetylacetonato)dichloro(1,5-cyclooctadiene)iridium(III), [$IrCl_2(C_5H_7O_2)(C_8H_{12})$]

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Abstract. $M_r = 470{\cdot}4$, orthorhombic, *Pnam*, $a = 13{\cdot}822\ (4)$, $b = 17{\cdot}117\ (5)$, $c = 11{\cdot}653\ (6)$ Å, $U = 2757{\cdot}0$ Å^3, $Z = 8$, $D_x = 2{\cdot}27$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 10{\cdot}36$ mm^{-1}, $F(000) = 1792$, $T = 133\ (2)$ K. Final $R = 0{\cdot}030$ for 2904 observed reflections. Mean bond lengths are Ir—Cl 2·348, Ir—O 2·022, Ir—C 2·182 and C=C 1·369 Å. The molecular dimensions are compared with those in acetylacetonato(1,5-cyclooctadiene)iridium(I).

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